



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Choong Paul Kim, et al.
Application No. : 10/735,148
Filed : December 12, 2003
Title : IN-SITU DUCTILE METAL/BULK GLASS MATRIX COMPOSITES
FORMED BY CHEMICAL PARTITIONING
Grp. /Div. : 1742
Examiner : George P. Wyszomierski.
Docket No. : 51667/RDS/C543

DECLARATION UNDER 37 C. F. R. 1.32

Assistant Commissioner for
Patents Washington, D.C. 20231

Post Office Box 7068
Pasadena, CA 91109-7068

Commissioner:

I, William L. Johnson, declare and state as follows:

1. I am the Ruben and Donna Metler Professor of Materials Science, Engineering, and Applied Science at the California Institute of Technology, Pasadena, California. I have been successively Assistant Professor, Associate Professor, and Professor of Materials Science at the California Institute of Technology since 1977. Before that, I was a post-doctoral Research Fellow at California Institute of Technology and at IBM, Thomas J. Watson Research Center.

2. I have a Bachelor of Arts Degree specializing in Physics from Hamilton College, Clinton, New York. I have a Ph.D. Degree in Applied Physics

I hereby certify that this correspondence is being deposited with the
U.S. Postal Service as first class mail in an envelope addressed to:
Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-
1450 am

11/11/05
(Date of Deposit)

Application No. 10/735,148

from the California Institute of Technology. My doctoral thesis related to amorphous metals and concerned graduate work under supervision of Professor Pol E. Duwez, one of the earliest investigators of amorphous metals.

3. I am a member of the U.S. National Academy of Engineering, a Fellow of ASM International, and a Fellow of the U.S. Metals, Minerals and Mining Society. I was the recipient of the 1998 Materials Research Society Gold Medal for research on metallic glasses. Other awards include the TMS/AIME Hume-Rothery Award for contributions to the "Science of Metal Alloys" for work on glass transformations; the ISMANAM Gold Medal for outstanding contributions to the field of metastable materials (bulk metallic glass materials); an Alexander Von Humboldt Foundation Distinguished Scientist Fellowship Award; and an Honorary Doctorate Degree in Physics from Bowling Green State University (Ohio).

4. A major part of my experience includes the study of rapidly quenched materials, disordered and amorphous solids, electronic structure of metals, ion beam induced modification of materials, superconducting materials, and phase transitions in solids. I and my colleagues were the first to study the superconducting properties of metallic glasses and the first examples of phase separation into two glassy phases of differing composition. We discovered and investigated the phenomena of crystal to glass transformations driven by solid state diffusion reactions. We have studied the relationship between melting, crystal to glass transformations, and the glass transition in undercooled liquids. We were involved in the first studies of production of nanocrystalline and amorphous materials by mechanical alloying.

5. We have developed several novel families of metallic alloys possessing superior glass-forming ability, which are also called "bulk metallic

Application No. 10/735,148

glasses". These glassy (or amorphous) alloys can be produced in "bulk" form from the melt by conventional casting without the need for rapid solidification. We have conducted the first studies of amorphous phase separation and its effect on stability and crystallization, determined time-temperature-transformation diagrams for crystallization from undercooled liquids, characterized the rheology of bulk glass-forming liquids, conducted the first studies of atomic diffusion in deeply undercooled metal alloys, and developed new metallic glass matrix composite materials which combine the unique mechanical properties of metallic glass with those of other engineering materials. Such composites have been demonstrated to exhibit "shear band pattern formation", which leads to dramatic enhancement of toughness, energy absorption, and other useful engineering properties of metallic glasses.

6. I have been and continue to be extensively involved in development of technical applications of bulk metallic glasses and metallic glass matrix composites, including collaborative research with several government and private industry laboratories. I co-founded Liquidmetal Technologies, a California company which specializes in development of metallic glasses as engineering and structural materials. I am currently Vice Chairman of the Board of Directors and Vice Chairman for Technology for Liquidmetal Technologies.

7. I am the inventor or co-inventor on over 25 patents and applications dealing with compositions, processing and technical applications of amorphous metals and amorphous metal composites. I am a co-inventor in the above-identified patent application and am thoroughly familiar with the invention described and claimed therein.

Application No. 10/735,148

8. I have presented more than six dozen invited talks, the majority of which deal with amorphous materials. I am the author or co-author of more than 370 technical papers and book chapters, most of which concern amorphous metals. I have supervised more than 80 doctoral candidates, post-doctoral fellows, visiting scientists, and visiting professors, with most of them being involved with some aspect of research and development of amorphous metals.

9. The above-identified patent application concerns formation of composite metal products having ductile crystalline metal particles in an amorphous metal matrix. An alloy is heated above the melting point of the alloy and cooled to or through a temperature between its liquidus and solidus. Upon cooling from the high temperature melt, the alloy chemically partitions, undergoing partial crystallization by homogeneous nucleation throughout the melt and subsequent growth of a crystalline phase in situ in the remaining liquid. Upon cooling the remaining liquid below the glass transition temperature, it freezes to an amorphous or glassy state, producing a two-phase microstructure containing crystalline particles or dendrites in an amorphous metal matrix.

10. Many metals can be cooled from the melt to a low temperature and remain in an amorphous state. Most such metals involve extremely fast cooling rates in the order of 10^4 to 10^6 °K/sec. Such rapid cooling rates mean that only relatively thin bodies of material may be kept amorphous since heat cannot be extracted quickly enough from thick bodies. In recent years, a variety of "bulk" metallic glass compositions have been developed which can remain amorphous when cooled at rates of 10^2 to 10^3 °K/sec. or even slower. A low critical cooling rate is highly desirable so that thick sections can be made in commercial products.

Application No. 10/735,148

11. A sometimes troublesome property of metallic glass (i.e., amorphous metal) is a lack of ductility, and the amorphous metal may fail catastrophically in shear. Ductility can be obtained in composites where a ductile phase is embedded in an amorphous metal matrix. The conventional way of making such a composite has been to infiltrate a pre-existing body (e.g., bundle of wires or mass of particles) with a glass-forming alloy composition. When this composite is cooled at less than the critical cooling rate to avoid crystallization, one obtains a composite material having a second phase (wires or particles) embedded in an amorphous metal matrix. Another way of forming a composite with particles distributed in an amorphous matrix is to disperse refractory metal particles in a molten alloy and cast or cool the two phase mixture to form a two phase composite. Surface reaction and crystallization may occur at the interface between the refractory metal particles and the matrix. However, the crystalline particles in the solid composite are principally the pre-existing particles in the mixture.

12. The technique described in the above-identified patent application produces a composite material having a ductile crystalline metal phase distributed in an amorphous metal matrix. This is obtained by cooling an alloy from the melt until a second phase forms in situ by homogeneous nucleation throughout the melt and followed by crystal growth. The technique may be used to produce composite materials with very fine dendrites spaced a short distance apart in the amorphous metal matrix. A composite prepared by such a process is different from a composite produced by infiltration into a preexisting mass of wires or particles. Generally, a composite made by such a process comprises

Application No. 10/735,148

particles of ductile crystalline metal formed in situ in an amorphous matrix rather than pre-existing wires or particles embedded in an amorphous matrix.

13. A remarkable, useful and unexpected property of such composites has been discovered. It is known that a glass-forming alloy has a certain "critical cooling rate". If the alloy is cooled from the melt faster than the critical cooling rate, it remains amorphous. If cooling is slower than the critical cooling rate, the metal crystallizes. An alloy may have a critical cooling rate of, for example, 10^3 °K/sec. when in bulk form or in a conventional composite. (If a metal embedded in a conventional composite has a high thermal conductivity, there may be a slightly lower apparent critical cooling rate. This is because the heat which must be extracted, can flow out of the composite faster than heat flows from the bulk glass-forming alloy alone. The magnitude of the change is related to the relative thermal conductivities and proportion of second phase in the amorphous matrix.)

14. It has been discovered that with composites formed by chemical partitioning according to the above-identified patent application, the critical cooling rate is lower by more than an order of magnitude than the critical cooling rate of a monolithic alloy having the composition of the amorphous metallic matrix. This effect is much larger than can be accounted for by relative thermal conductivities. The very fine structure produced by homogeneous nucleation and growth of crystals from the molten alloy is believed to be responsible for suppressing the crystallization of the remaining liquid.

15. Crystallization may occur in glass-forming metals by nucleation in the melt and subsequent crystal growth. Crystallization is not instantaneous, and progresses as a crystallization front propagating through the amorphous

Application No. 10/735,148

material, which may still be considered a liquid (or super-cooled liquid). I believe that the very fine spacing between the previously precipitated crystals in the composite material described in this application creates a tortuous path through which the crystallization front must propagate in the remaining liquid. Because of this, whatever nucleation occurs in the remaining melt as it is cooled has influence over a very short distance. A crystallization front through the glass-forming melt is severely inhibited and most of the matrix remains amorphous in the final composite.

16. We have observed sufficient inhibition that the critical cooling rate for a composite material is more than an order of magnitude less than the critical cooling rate for a monolithic liquid alloy having the same composition as the matrix. This very useful effect in the composites produced according to this application was surprising and completely unexpected. Because the critical cooling rate is much lower, than for composites formed by infiltration or casting of mixtures of liquid and crystals, much thicker composite bodies may be formed.

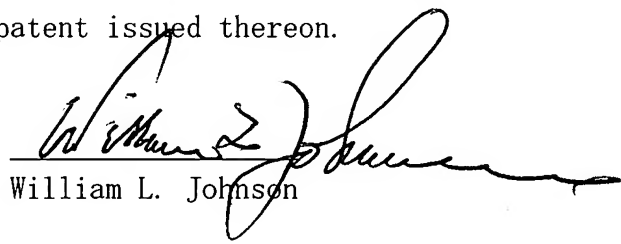
17. In addition, a composite having ductile metal particles precipitated in situ in an amorphous metal matrix exhibits ductility that is not present in a bulk metallic glass. Patterns of shear bands propagate through the amorphous metal matrix and through the ductile dendrites to produce overall ductility in the composite.

18. I am a coauthor or co-inventor and am familiar with the Choi-Yim, Lin and Dandliker references cited of record in the above identified application. None of the composites mentioned in any of these references have particles that are formed in situ in an amorphous metal matrix. Composites mentioned in these references are formed by infiltration of glass-forming alloy into pre-existing

Application No. 10/735,148

particles (or wires) or casting of mixtures of particles in a molten glass-forming alloy.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.



William L. Johnson

RDS/mas

RDS PAS649121.1-*--11/1/05 11:03 AM